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CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF
HARVARD COLLEGE.

ON CERTAIN DERIVATIVES OF SYMMETRICAL
TRICHLORBENZOL.

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IN a paper by Sidney Calvert and one of us,* the behavior of tribromiodbenzol $\text{Br}_3\text{I},\text{3},\text{5},\text{I}2$, and of tetrabrombenzol $\text{Br}_4\text{I},\text{2},\text{3},\text{5}$, with sodic ethylate was studied, and it was shown that the atom of iodine (or the atom of bromine in the corresponding position) was replaced by hydrogen under these conditions, giving the symmetrical tribrombenzol. It seemed of interest in this connection to study the corresponding trichlor compounds, that is, the trichloriodbenzol and the trichlorbrombenzol, to see whether the loosening effect of the three chlorine atoms might not be even greater than that of the three atoms of bromine, and thus make it possible that these substances would react with other agents beside sodic alcoholates, which were the only reagents that had any such effect upon the bromine compounds.

At that time it was not worth while to undertake the work, because of the great difficulty in preparing symmetrical trichloraniline, but since this obstacle has been removed by the beautiful method of Victor Meyer and Sudborough,† we have prepared these compounds and studied some of their relations. Trichloriodbenzol, $\text{Cl}_3\text{I},\text{3},\text{5},\text{I}2$ melts at 55° ; and by treatment with sodic ethylate dissolved in alcohol and benzol yielded symmetrical trichlorbenzol recognized by its melting point 64° and two analyses. It therefore behaved like the tribromiodbenzol under these conditions. All our other attempts to obtain a simple replacement of the iodine in this substance failed, so that it is no more reactive than the tribromiodbenzol. Fuming nitric acid converted the trichloriodbenzol into the trichlorodinitrobenzol melting at 129° , iodine being set free.

* These Proceedings, XXXI. 123.

† Ber. d. chem. Ges., XXVII. 3151.

The trichlorbrombenzol $\text{Cl}_3\text{C}_6\text{H}_2\text{Br}_2$ melts at 65° , that is, at nearly the same temperature as the symmetrical trichlorbenzol $63^\circ.4$ (Körner), and what is strange, higher than the corresponding trichloriodbenzol. With sodic ethylate it lost bromine, but the reaction was not specially studied. When treated with fuming nitric acid it gave a trichlorbrom-dinitrobenzol melting at 175° , which was a decidedly reactive substance. Aniline replaced the three atoms of chlorine, giving the trianilidobrom-dinitrobenzol $\text{C}_6(\text{C}_6\text{H}_5\text{NH})_3\text{Br}(\text{NO}_2)_2$, melting at 175° to 176° , discovered by W. D. Bancroft and one of us.*

Sodic ethylate also acts upon it, probably giving a number of products, to judge from analogy and the fact that both sodic bromide and sodic nitrite were detected among them, but we have only succeeded in identifying one of these with certainty; this is a bromdinitroresorcine diethyl-ether melting at 81° to 82° , and probably having the following constitution, $(\text{OC}_2\text{H}_5)_2\text{C}_6\text{H}_2\text{Br}_2(\text{NO}_2)_4,6$, although it may be that one of the ethoxy groups stands at 5 instead of 3. It must have been formed by the replacement of two atoms of chlorine by two ethoxy groups, and the third by hydrogen. As in most of the replacements of a halogen by hydrogen it has been found that it stood between two nitro groups, we think there can be little doubt that the first constitution assigned to this body is the correct one. Its formation is interesting, as it is the first case we have found in which chlorine has been replaced by hydrogen under these conditions. In all the other cases studied the chlorine has remained unaltered, or has entered into some simple reaction: thus picrylchloride gave picryl ether,† picrylmalonic ester,‡ or picrylacetacetic ester,§ according to the reagent used; chloranil gave dichlorquinonedimalonic ester,|| or, so far as the replacement alone was concerned, dichloridethoxyquinone;¶ and trichlorodinitrobenzol gave dichlorodinitrophenyl-malonic ester,|| or chlordinitroresorcine diethylether, and dinitrophloroglucine triethylether.||† These last cases are especially striking, since the corresponding tribromdinitrobenzol showed a replacement of bromine by hydrogen, when treated with sodium malonic ester or sodic ethylate.

* These Proceedings, XXIV. 293.

† Jackson and Boos, These Proceedings, XXIII. 176.

‡ Jackson and Soch, *Ibid.*, XXX. 401.

§ Dittrich, *Ber. d. chem. Ges.*, XXIII. 2720.

|| Stieglitz, *Am. Chem. Journ.*, XIII. 38.

¶ Kehrmann, *J. prakt. Chem.*, [2], XL. 367; Jackson and Grindley, These Proceedings, XXX. 430.

||† Jackson and Lamar, *Am. Chem. Journ.*, XVIII. 775.

‡ The same, *Ibid.*, p. 668.

This bromdinitroresorcine diethylether, melting at 81°–82°,
 $(OC_2H_5)_21,3,Br2,(NO_2)_24,6?$
 is isomeric with those melting at 184°,
 $(OC_2H_5)_21,5,Br3,(NO_2)_22,4,$
 and at 92°,
 $(OC_2H_5)_21,3,Br5,(NO_2)_22,4,$
 made by the action of sodic ethylate on the symmetrical tribromdinitrobenzol.

The trichlorbromdinitrobenzol also reacted with sodium malonic ester but we were unable to bring the product into a state fit for analysis. When the dry substance was treated with sodic ethylate, it gave a deep vermillion product, which probably belongs to the class of colored compounds formed by sodic ethylate and certain nitro bodies,* as it was decomposed by water and some organic solvents. This is the first case, so far as we can find, in which one of these substances has been observed derived from a compound of benzol with all its atoms of hydrogen replaced by other radicals.

Trichloriodbenzol, $C_6H_2Cl_3I$.

To prepare this substance 17 grams of sublimed trichloraniline (made by the excellent method of V. Meyer and Sudborough †) were mixed with moderately dilute sulphuric acid in the proportion of one molecule of trichloraniline to each molecule of sulphuric acid, and after thorough cooling powdered sodic nitrite was added in small successive quantities, until the nitrous fumes generated were no longer absorbed. After each addition of the sodic nitrite the flask was corked and vigorously shaken, until all the red fumes were absorbed, taking care that the contents were kept cool throughout the operation. When a sufficient amount of sodic nitrite had been added, the mixture was filtered, the cooled filtrate freed as completely as possible from the excess of nitrous fumes by vigorous shaking, and then treated with a distilled aqueous solution of hydriodic acid, until there was no further action. The brownish precipitate thus obtained was washed first with a solution of potassic iodide to remove free iodine, and finally with water, after which it was purified by sublimation, or by crystallization from hot alcohol, until it showed the constant melting point of 55°. It was dried *in vacuo*, and gave the following results on analysis:—

* These Proceedings, XXXIII. 173, and Amer. Chem. Journ., XIX. 199, where a complete list of the papers on this subject is given.

† Ber. d. chem. Ges., XXVII. 3151.

0.2188 gram of the substance gave by the method of Carius 0.4746 gram of a mixture of argentic chloride and iodide. After washing this precipitate with ammonic hydrate 0.1672 gram of argentic iodide were left undissolved.

	Calculated for $C_6H_2Cl_3I$.	Found.
Chlorine and Iodine	75.94	76.10
Chlorine	34.69	34.73
Iodine	41.30	41.29

The substance is therefore trichloriodbenzol, and as it was made from common trichloraniline its constitution must be Cl_3I_3 .

Properties of Trichloriodbenzol. — It crystallizes from alcohol in white slender needles terminated by one plane at a very acute angle; these needles are often a centimetre or more long, and are much branched, the branches forming a sharp angle with each other and developing into forms like feathers. It melts at 55° , and sublimes easily. It is freely soluble in ether, benzol, chloroform, acetone, carbonic disulphide, or ligroin; soluble in ethyl or methyl alcohol, when cold, more freely soluble when hot; soluble in glacial acetic acid; insoluble in water, cold or hot. A mixture of alcohol and chloroform is the best solvent for it. It is apparently unaffected by the strong acids, or by sodic, potassic, or ammonic hydrate.

Behavior of Trichloriodbenzol with Sodic Ethylate.

Two grams of trichloriodbenzol dissolved in anhydrous benzol were mixed with 20 c.c. of an alcoholic solution of sodic ethylate made from one gram of sodium, and the mixture was allowed to stand over night. The liquid turned dark brown, and a precipitate began to separate soon after adding the ethylate. To make certain that the reaction was complete, the mixture was heated on the steam bath in a flask with a return condenser, which rendered the brown color much darker. The product was then evaporated to dryness; during the evaporation an odor like that of an aldehyd was observed, but the presence of one could not be determined by other tests. The dry residue was treated with water, and the insoluble portion separated from the solution, which gave tests for an iodide. The portion insoluble in water, which was very dark brown, was washed thoroughly, and then purified by crystallization from alcohol, until it showed the constant melting point 64° , which proved that it was the symmetrical trichlorbenzol. This was confirmed by the following analyses of the substance dried *in vacuo* : —

- I. 0.0906 gram of the substance gave by the method of Carius 0.2154 gram of argentic chloride.
 II. 0.0792 gram of the substance gave 0.1862 gram of argentic chloride.

	Calculated for $C_6H_3Cl_3$.	Found.	
		I.	II.
Chlorine	58.68	58.78	58.13

Behavior of Trichloriodbenzol with Other Reagents.

With aniline even at its boiling point trichloriodbenzol showed no signs of action, except that the color of the mixture became darker, and a certain amount of turbidity appeared, but no test for an iodide could be obtained, and the trichloriodbenzol was recovered unaltered.

When trichloriodbenzol was heated on the steam bath for three hours with an aqueous solution of sodic hydrate, the liquid took on a chrome-yellow color, but this must have been due to a very slight reaction, as after acidification it gave no precipitate with argentic nitrate, and essentially the whole of the trichloriodbenzol was recovered unaltered.

Melted sodic hydrate, on the other hand, seemed to act upon it, as a brownish mass was obtained, which after solution in water gave a slight precipitate on acidification and a reddish solution; a good test for an iodide was obtained, but the yield of the new organic substance was so small that we did not study this reaction further, since at best it seemed to us of slight interest.

Sodium malonic ester had little or no action on the trichloriodbenzol, most of which was recovered unaltered from the product, so that the hope of obtaining enough of a substance (if one were really formed) for analysis was so small that we did not continue work in this line.

From these experiments it appears that the trichloriodbenzol is no more reactive than the tribromiodbenzol, from which exactly similar results were obtained by Sidney Calvert and one of us.*

When trichloriodbenzol was mixed with nitric acid of specific gravity 1.50 and strong sulphuric acid, and the mixture gently heated, the solid went into solution. It was allowed to stand at ordinary temperatures over night, and then precipitated with a large quantity of water, when a mixture of a white body and scales of iodine was thrown down. The iodine was recognized by its crystalline form, color, smell, and purple fumes. The white body was purified by crystallization from alcohol,

* These Proceedings, XXXI. 128.

when it showed the melting point 129° , and is therefore the trichlor-dinitrobenzol $\text{Cl}_3\text{I}, 3, 5, (\text{NO}_2)_2, 2, 4$.

Trichlorbrombenzol $\text{C}_6\text{H}_2\text{Cl}_3\text{Br}$.

Twenty grams of trichloraniline dissolved in 100 c.c. of hot glacial acetic acid were mixed with 90 c.c. of hydrobromic acid (boiling at 125°), and, disregarding the heavy grayish yellow precipitate, the mixture was thoroughly cooled in an ice bath, and then treated with powdered sodic nitrite, until red fumes were given off freely. The sodic nitrite was added in small quantities at a time, and the flask containing the mixture shaken vigorously after each addition, the liquid being kept cool throughout. The heavy precipitate already mentioned went into solution during the addition of the sodic nitrite, forming a dirty yellow liquid. After standing for a few hours to complete the reaction, the contents of the flask were poured into an evaporating dish, and heated for an hour on the steam bath. In this way a dark oily product floating on the surface of the liquid was obtained, which solidified on cooling. The mother liquor deposited more of this product in a semi-crystalline condition, and an additional amount was obtained from it by heating it again with more hydrobromic acid. The product was purified by sublimation followed by recrystallization from alcohol, until it showed the constant melting point $64^{\circ}-65^{\circ}$. As this is the same as the melting point of trichlorbenzol, we supposed at first that our product was this body, but the following analyses of the substance dried *in vacuo* showed that it was the desired trichlorbrombenzol.

- I. 0.1618 gram of the substance gave by the method of Carius 0.3850 gram of the mixture of argentic chloride and bromide.
- II. 0.1116 gram of the substance gave 0.2656 gram of the mixture of argentic chloride and bromide.
- III. 0.1276 gram of the substance gave on combustion 0.1274 gram of carbonic dioxide and 0.0108 gram of water.

	Calculated for $\text{C}_6\text{H}_2\text{Cl}_3\text{Br}$.	Found.		
		I.	II.	III.
Chlorine and Bromine *	71.60	71.76	71.74	
Carbon	27.64			27.23
Hydrogen	0.77			0.94

* By a curious coincidence the results of analyses I. and II., if calculated as argentic chloride, give numbers agreeing excellently with the percentages calculated for $\text{C}_6\text{H}_2\text{Cl}_3$, so that the combustion was necessary to determine whether our compound was this, or the $\text{C}_6\text{H}_2\text{Cl}_3\text{Br}$ which has the same melting point.

The yield of trichlorbrombenzol was 12 grams, instead of the 26.5 grams which should have been obtained from 20 grams of trichloraniline, that is, over 45 per cent of the theory.

Properties of Trichlorbrombenzol. — It crystallizes from alcohol in white radiating needles, which develop into long slender blunt ended prisms. It melts at 64° – 65° , that is, one degree higher than the symmetrical trichlorbenzol, which melts according to Körner at $63^{\circ}.4$; not only is this coincidence striking, but it is also surprising that it should melt at a higher temperature than the trichloriodbenzol, which melts at 55° . It sublimes easily. It is freely soluble in ether, benzol, or acetone; soluble in cold alcohol, more freely in hot; soluble in glacial acetic acid, or ligroin; less soluble in methyl alcohol, and still less in carbonic disulphide. The best solvent for it is alcohol. The three strong acids have no apparent action on it, but fuming nitric acid converts it into trichlorbromdinitrobenzol, as described later. When a benzol solution of the trichlorbrombenzol was treated with sodic ethylate, the atom of bromine was removed, as was shown by testing the wash waters from the product for bromine, when a strong reaction for it was observed.

Trichlorbromdinitrobenzol $C_6Cl_3Br(NO_2)_2$.

To prepare this substance the trichlorbrombenzol was mixed with nitric acid of specific gravity 1.52 and one third the quantity of strong sulphuric acid, and the mixture heated gently for an hour. At first the solid dissolved, but later the nitro compound was deposited from the solution. After the mixture had stood over night, the supernatant acid was poured into a large quantity of water, which gave an additional amount of the product. It was purified by crystallization from a mixture of alcohol and benzol, until it showed the constant melting point 175° , when it was dried *in vacuo*, and analyzed with the following result: —

0.1654 gram of the substance gave according to the method of Carius
0.2914 gram of the mixture of argentic chloride and bromide.

	Calculated for $C_6Cl_3Br(NO_2)_2$.	Found.
Bromine and Chlorine	53.21	53.10

The constitution of this substance is settled by the method, in which it was made as $Cl_3C_6H_3Br_2(NO_2)_2$. The yield is essentially quantitative.

Properties of Trichlorbromdinitrobenzol. — It forms, when crystallized
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from alcohol and benzol, thick rather blunt rhombic plates, the obtuse angles of which are frequently bevelled by two planes. They show a tendency to form groups with the members superimposed, and have a slight yellowish tinge. The substance melts at 175° ; and is very soluble in chloroform, acetone, or carbonic disulphide; slightly soluble in ethyl or methyl alcohol either cold or hot; insoluble in cold, soluble in hot glacial acetic acid; essentially insoluble in ligroin, or in hot or cold water. The best solvent for it is a mixture of benzol and alcohol. Strong hydrochloric or sulphuric acid has no apparent action on it. Fuming nitric acid dissolves it when hot. It sublimes easily, and in this way feathery ivory-white crystals are obtained sometimes over a centimeter in length.

Action of Aniline on Trichlorbromdinitrobenzol.

When one gram of trichlorbromdinitrobenzol was warmed gently with a slight excess of freshly distilled aniline, it went into solution forming a cherry-red liquid, the color of which became deeper on longer heating. To obtain the product the liquid was poured into a large quantity of water, acidified with hydrochloric acid, and the crimson precipitate formed in this way thoroughly washed, and crystallized from a mixture of alcohol and benzol, until it reached the constant melting point 175° – 176° . This showed that the substance was the bromodinitrotrianilidobenzol $C_6Br(NO_2)_2(C_6H_5NH)_3$ obtained by W. D. Bancroft and one of us* from tetrabromdinitrobenzol and aniline. In this case it was formed by the replacement of the three atoms of chlorine by three anilido groups.

Behavior of Trichlorbromdinitrobenzol with Sodic Ethylate in the Cold.

Five grams of trichlorbromdinitrobenzol dissolved in anhydrous benzol were mixed with the sodic ethylate made from twenty-five grams of absolute alcohol and one gram of sodium, which gave the proportion of three molecules of the ethylate to each molecule of trichlorbromdinitrobenzol. The two substances reacted at once, since the liquid took on a bright scarlet color as soon as they were mixed, and there was also a slight evolution of heat. To complete the reaction the mixture was allowed to stand three days at ordinary temperatures, during which time a heavy precipitate was deposited, and the color changed to a yellowish red. The precipitate was filtered out, washed with alcohol, and then dissolved in water. This solution gave a strong test for sodic nitrite with

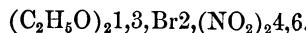
* These Proceedings, XXIV. 293.

potassic iodide, starch paste, and dilute sulphuric acid, and also a heavy white precipitate with argentic nitrate and nitric acid. To obtain the organic products of the reaction the reddish alcoholic filtrate was allowed to evaporate spontaneously, and the residue treated with water; the insoluble substance thus obtained was purified by crystallization from alcohol, until it showed the constant melting point 81° – 82° , when it was dried *in vacuo*, and analyzed with the following result:—

- I. 0.1236 gram of the substance gave by the method of Carius 0.0684 gram of argentic bromide.
 II. 0.2500 gram of the substance gave 18.4 c.c. of nitrogen at a temperature of 23° and a pressure of 754.7 mm.

	Calculated for $C_6HBr(C_2H_5O)_2(NO_2)_2$	Found.	
		I.	II.
Bromine	23.89	23.56	
Nitrogen	8.36		8.24

The substance is therefore a bromdinitroresorcine diethylether formed from the trichlorbromdinitrobenzol by the replacement of two atoms of chlorine by ethoxy groups, and of the third by hydrogen. Certain points in regard to its constitution are settled, since the two ethoxy groups must be in the meta position to each other, and the atom of bromine and the two nitro groups are in the symmetrical position to each other. The radicals therefore are probably arranged as follows,



but it is possible that one of the ethoxy groups instead of the atom of hydrogen stands at 5 between the two nitro groups. It is isomeric with the bromdinitroresorcine diethylether melting at 184° , and made by Warren and one of us* from tribromdinitrobenzol and sodic ethylate in the cold, which has the constitution $(C_2H_5O)_21,5,Br3,(NO_2)_24$, and also with that melting at 92° obtained by Koch and one of us,† as another product from the same reaction, which has the constitution



The yield of the bromdinitroresorcine diethylether was one gram from five of the trichlorbromdinitrobenzol, that is, about 21 per cent of the theoretical yield.

* These Proceedings, XXV. 166.

† These Proceedings, XXXIV. 128.

Properties of Bromdinitroresorcine Diethylether, melting at 81°-82°,
 $C_6H(C_2H_5O)_2Br(NO_2)_2$.

It forms when crystallized from alcohol white needles or slender prisms terminated by two planes at an obtuse angle to each other, which turn brown on exposure to the light. It melts at 81°-82°, and is very soluble in benzol, or chloroform; soluble in methyl alcohol, acetone, glacial acetic acid, or carbonic disulphide; slightly soluble in cold ethyl alcohol, more soluble in hot; slightly soluble in ligroin. Alcohol is the best solvent for it. It is not acted on apparently by strong hydrochloric acid, either hot or cold; strong sulphuric acid does not act in the cold, but when warm dissolves it with a brownish red color; strong nitric acid does not act in the cold, but gives a colorless solution with it when hot.

That this bromdinitroresorcine diethylether was not the only organic product of the reaction of sodic ethylate on trichlorbromdinitrobenzol was shown by the fact that sodic nitrite as well as sodic chloride was formed. Our attempts to isolate these other bodies, however, were far from successful. Some experiments with the aqueous wash waters seemed to indicate that they contained a phenol melting at 111°, and having perhaps the formula $C_6(OC_2H_5)_2OH(NO_2)_2Br$, but the analytical data obtained were too imperfect to justify a description of the body; and we did not succeed in bringing any of the other products into a state fit for analysis.

The trichlorbromdinitrobenzol seemed to give colored compounds with sodic ethylate similar to those given by picrylch oride and several other nitro compounds, since upon adding an alcoholic solution of sodic ethylate to the dry substance it took on a strong vermillion color, which was instantly destroyed by water, and more slowly by benzol or ligroin. The fact that the color disappeared on the addition of water indicates that it is one of the colored compounds under discussion, and not a salt of a phenol. Another sample of the color was allowed to stand for half an hour exposed to the air, at the end of which time the red color had given place to yellow. As the colored compound was less stable than several others which have been studied, its investigation was not carried further.

The trichlorbromdinitrobenzol is acted on by an alcoholic solution of sodium malonic ester. Our first experiments gave a crystalline product, but in too small quantity for analysis. Our later experiments have yielded only viscous masses, from which we have not succeeded in obtaining anything for analysis in spite of a very large expenditure of time and material.